CONTRIBUTION FROM THE WESTERN RESEARCH CENTER,
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The Difluorochlorinium(III) Cation, ClF_2^+. Vibrational Spectra and Force Constants

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Received July 11, 1966

The vibrational spectra of $ClF_2^+AsF_6^-$ (infrared and Raman) and $ClF_2^+BF_4^-$ (infrared) have been recorded. All fundamentals have been observed. The previously reported infrared spectrum is incomplete and its assignment is erroneous. The ionic character of the complexes and the bent structure of the ClF_2^+ cation (point group C_{2v}) are confirmed. Strong crystal field effects occur in both complexes. A complete set of force constants based on a valence force field is calculated with the revised normal vibrations. The bent structure of ClF_2^+ is further supported by the small observed difference between the two stretching vibrations and by force constant and bond order considerations. The F–Cl–F bond angle can be limited to a range of 90–120°. Although the valence force constant of ClF_2^+, 4.77 ± 0.07 mdynes/A, is somewhat higher than that of ClF, their bond orders are identical. Comparison of the valence force constants and bond orders of ClF_2^+, ClF_2^-, and ClF indicates their usefulness for distinguishing semiionic three-center–four-electron bonds from localized covalent bonds. The localized covalent p–σ bond model is considered most likely for ClF_2^+.

Introduction

The relatively stable 1:1 adducts formed by the interaction of ClF_3 and a strong Lewis acid, such as AsF_5 or SbF_5, were first prepared in 1950.[2] This work, however, has never been published owing to classification. A few years later the same compounds were independently prepared in Hungary,[3] but again this work was not published. The first publications on these complexes[4,5] described the $ClF_3 \cdot AsF_5$ and $ClF_3 \cdot SbF_5$ adducts. Later, $ClF_3 \cdot PtF_5$,[6] $ClF_3 \cdot BF_3$,[7] and $ClF_3 \cdot PF_5$[8] were prepared. It was suggested[3–5,7] that these types of complexes were ionic and contained the ClF_2^+ cation. We[8] have recently established this. A bent structure (point group C_{2v}) for the ClF_2^+ cation, based on the infrared spectra of $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$, has also been proposed.[8]

The results obtained from the investigation of the Raman spectra of several chlorine fluoride based complexes[9,10] were in good agreement with the corresponding infrared data[11–13] except for the ClF_2^+ cation. Therefore, we decided to reexamine the infrared spectra of $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$.

Experimental

Materials.—The materials used in this work were manipulated in a standard Pyrex high-vacuum system which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Chlorine trifluoride and BF_3 (both from the Matheson Co., Inc.) and AsF_5 (Ozark Mahoning Co.) were purified by several low-temperature vacuum distillations. Chlorine trifluoride was always treated for several hours with NaF to remove any HF impurity. Little etching could be observed in the vacuum line. The purity of the volatile compounds was determined by measurements of their vapor pressures, molecular weights, and infrared spectra. Outside the vacuum system, materials were handled in the dry nitrogen atmosphere of a glove box.

Infrared Spectra.—Infrared spectra were recorded on a Beckman Model IR-9 prism-grating spectrophotometer in the range 4000–400 cm^{-1}. The low-temperature spectra of $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$ were taken by condensing the complex onto internal AgCl plates (cooled with liquid nitrogen) of a Pyrex infrared cell equipped with AgCl end windows. Screw-cap metal cells with AgCl windows and neoprene O rings were used for obtaining the spectrum of $ClF_2^+AsF_6^-$ as a dry powder at ambient temperature.

Raman Spectra.—The Raman spectra were recorded on a Cary Model 81 spectrophotometer, using the blue mercury line (4358 A) as exciting line and a saturated KNO_2 solution as filter. Pyrex tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses were used as sample cells.

Preparation of $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$.—The preparation of both these complexes has previously been described.[8]

Results

$ClF_2^+AsF_6^-$. Vibrational Spectra.—The low-temperature and ambient-temperature infrared spectrum and the Raman spectrum of $ClF_2^+AsF_6^-$ are shown in Figures 1 and 2, respectively. Because of the strong background resulting from the dry powder technique, the resolution of the room-temperature infrared spectrum in the range 680–450 cm^{-1} is poor. The absence of solid ClF_3 or AsF_5 in the low-temperature infrared spectrum can be readily established by comparison with the spectra previously reported[8] for these compounds. In addition, the room-temperature infrared spectrum supports these results, since solid AsF_5 (boiling point of AsF_5 is −53°) could not be present at this temperature and atmospheric pressure. Therefore, the absorption at 818 cm^{-1} is due to $ClF_2^+AsF_6^-$ and not to solid AsF_5 (strong absorption at 814 cm^{-1}). Table I lists the observed frequencies of the infrared and Raman spectra of $ClF_2^+AsF_6^-$.

$ClF_2^+BF_4^-$. Infrared Spectrum.—Figure 3 shows the low-temperature infrared spectrum of $ClF_2^+BF_4^-$. The observed frequencies are listed in Table I. The absence of both starting materials, *i.e.*, ClF_3 and BF_3, in

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[1] Visiting Scientist from the Institut für Anorganische Chemie, Technische Hochschule, Stuttgart, Germany.

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[9] K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, in press.

[10] K. O. Christe and W. Sawodny, to be published.

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[12] K. O. Christe and J. P. Guertin, *ibid.*, **4**, 1785 (1965).

[13] K. O. Christe and J. P. Guertin, *ibid.*, **5**, 473 (1966).

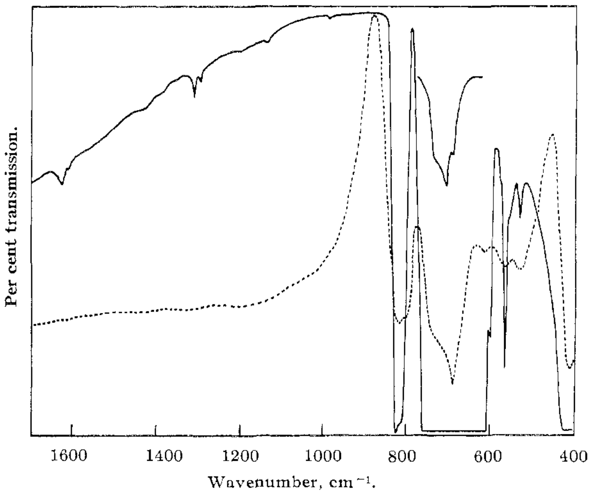

Figure 1.—The infrared spectra of solid $ClF_2^+AsF_6^-$: ———, low-temperature spectrum; --------, at 25° by dry powder technique.

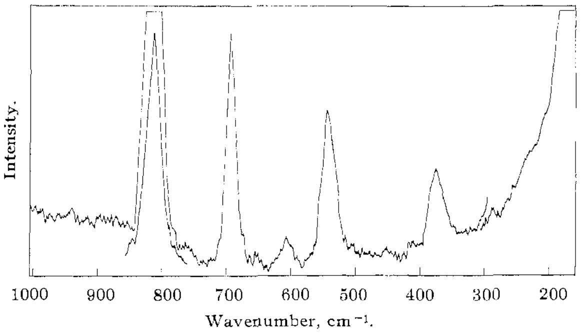

Figure 2.—Raman spectrum of $ClF_2^+AsF_6^-$.

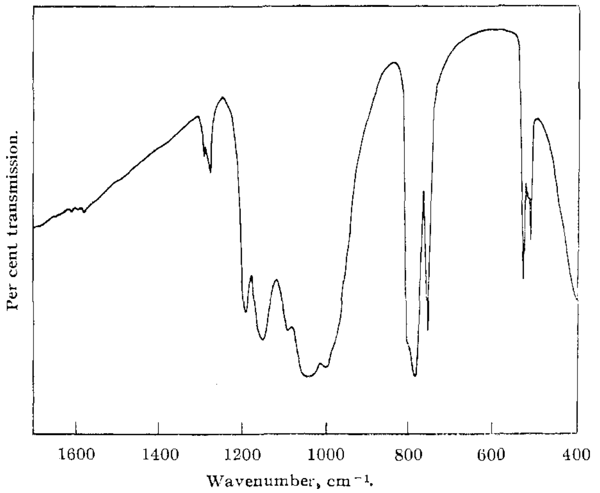

Figure 3.—Low-temperature infrared spectrum of $ClF_2^+BF_4^-$.

the spectrum was confirmed by comparison with the reported infrared absorption of solid ClF_3[8] and solid BF_3.[14] The Raman and room-temperature infrared spectra of the complex were not recorded owing to its considerable dissociation pressure (760 mm at 9°).[7]

Calculation of Force Constants.—For the calculation of force constants for ClF_2^+ (symmetry C_{2v}) the G and F matrices were set up according to the method of Wilson, Decius, and Cross,[15] assuming a valence force field. For the solution of the secular equation, a recently published method[16] was used. This allowed the calculation of a complete set of force constants without additional data except for the normal frequencies. Since four constants were calculated from only three frequencies, the method must be considered as an approximation. However, a good approximation of the values of the general valence force field was obtained for a number of bent XY_2 molecules.[17] No exact structural data are known for ClF_2^+. However, the value of the F–Cl–F angle is expected to have a strong influence on some of the potential constants. The force constants calculated for eight different angles are listed in Table II. For this calculation a mean value of the two infrared bands (558 and 520 cm^{-1}) and of the Raman line (544 cm^{-1}) was used. If 520 cm^{-1} is assumed to be the frequency value of the deformation mode, the following variations occur: f_r, +0.03; f_{rr}, +0.03; $f_{r\alpha}$, −0.006 to 0; and f_α, −0.12 to −0.09 mdyne/A.

Table I

Vibrational Spectra of $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$ and Their Assignment

Frequencies obsd, cm⁻¹, intensity: $ClF_2^+AsF_6^-$ Infrared	$ClF_2^+AsF_6^-$ Raman	$ClF_2^+BF_4^-$ Infrared	Assignment (point group): $ClF_2^+(C_{2v})$	$AsF_6^-(O_h)$	$BF_4^-(T_d)$
1624 1610 } vw		1610 1575 } vw	$\nu_1 + \nu_3$ and $2\nu_3$, $2\nu_1$		
1312 1297 } vw				$\nu_2 + \nu_4$	
		1305 1289 } vw			$\nu_1 + \nu_4$
		1145–978 vs, b			ν_3 (F_2)
1130 vw					
976 vw					
818 s		813 sh	ν_3 (B_1)		
810 sh	811 vs	798 s	ν_1 (A_1)		
		766 m			ν_1 (A_1)
703 vs				ν_4 (F_{1u})	
	693 s			ν_1 (A_{1g})	
609 w	603 vw			ν_2 (E_g)	
558 m 520 w }	544 m	537 ms	ν_2 (A_1)		
		529 sh			ν_4 (F_2) B^{10}
		519 m			ν_4 (F_2) B^{11}
406 m				ν_3 (F_{1u})	
	375 mw			ν_5 (F_{2g})	

Table II

Calculated Force Constants for the ClF_2^+ Cation (Assuming Different F–Cl–F Angles)

F–Cl–F angle, deg	Force constants, mdynes/A: f_r	f_{rr}	$f_{r\alpha}$	f_α
90	4.706	−0.170	0.140	1.296
95	4.705	−0.026	0.139	1.256
100	4.714	0.118	0.135	1.216
105	4.732	0.261	0.129	1.176
109° 27′	4.756	0.389	0.122	1.141
115	4.794	0.546	0.111	1.098
120	4.839	0.688	0.100	1.060
180	5.486	1.873	0	0.793

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Discussion

In a previous paper[8] we have reported the infrared spectra of $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$. We assigned the bands at 558 and 534 cm^{-1} to the antisymmetric stretching vibration of ClF_2^+ and the bands at 520 and 515 cm^{-1} to the symmetric stretching vibration. However, our present investigation of the vibrational spectra of chlorine fluoride based complexes indicated that this assignment might be incorrect for the following two reasons: (i) The Raman spectrum of $ClF_2^+AsF_6^-$ has its strongest line at 811 cm^{-1}. This line should be assigned to the symmetric Cl–F stretching vibration of ClF_2^+. (ii) The absorptions in the range 560–515 cm^{-1} are occurring at wavenumbers too low for stretching vibrations in this type of complex. One would expect the Cl–F bonds of ClF_2^+ to be similar in nature to those of ClF, the positive charge on the central atom perhaps increasing the Cl–F stretching frequency to some extent. Therefore, the expected range for the Cl–F stretching vibrations for ClF_2^+ would be 750–850 cm^{-1}. The strong band in the $ClF_2^+BF_4^-$ spectrum at 798 cm^{-1} which had not been assigned previously[8] further supports this view.

A careful reinvestigation of the infrared spectrum of $ClF_2^+AsF_6^-$ at low temperature and at 25° showed that the previously reported spectrum of $ClF_2^+AsF_6^-$ is incomplete. The band at 818 cm^{-1} with a shoulder at 810 cm^{-1}, the latter coinciding with a strong Raman line, is due to ClF_2^+. These frequencies agree well with the expected range for the antisymmetric and symmetric stretching vibrations.

The observed vibrational spectra of $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$ are listed in Table I together with their assignments. The vibrations belonging to AsF_6^- and BF_4^- will be dicussed first, since they can be assigned more easily by comparison with similar complexes containing these anions. An octahedral anion of the type XY_6^- has O_h symmetry. The six normal modes of vibration are classified as $(A_{1g} + E_g + 2\,F_{1u} + F_{2g} + F_{2u})$. Of these, only the two F_{1u} modes will be infrared active, while the A_{1g}, E_g, and F_{2g} modes will be only Raman active. The remaining F_{2u} mode is inactive in both the infrared and the Raman spectrum, provided that the selection rules are valid and that the octahedron is not distorted. By comparison with the vibrational spectra of $K^+AsF_6^-$,[18] $AsCl_4^+AsF_6^-$,[19] and $NF_4^+AsF_6^-$,[20] the normal modes belonging to AsF_6^- can be assigned without difficulty. All five expected normal modes were observed, the symmetric stretching vibration (ν_2, E_g) being somewhat uncertain in the Raman spectrum owing to its low intensity. The observed frequencies and intensities are in good agreement with that of the above-mentioned AsF_6^--containing complexes.

A tetrahedral anion of the type XY_4^-, such as BF_4^-, has T_d symmetry. The four normal modes of vibration are classified as $(A_1 + E + 2\,F_2)$. Of these only the two F_2 modes are expected to be infrared active. However, crystal field effects or slight distortion of the BF_4^- tetrahedron can result in the A_1 mode also becoming infrared active. The bands in the spectrum of $ClF_2^+BF_4^-$ due to BF_4^- can be assigned by comparison with the spectra of $ClF_2^+AsF_6^-$ and $K^+BF_4^-$.[21–23] Obviously the broad band of high intensity centered at about 1030 cm^{-1} is the antisymmetric stretching vibration, ν_3. The antisymmetric deformation vibration, ν_4, is expected to show isotope splitting.[21] The band at 519 cm^{-1} is assigned to ν_4 of $B^{11}F_4^-$, while ν_4 of $B^{10}F_4^-$, which should occur at a somewhat higher frequency and be of lower intensity, is most likely the shoulder observed at 529 cm^{-1}. The band at 537 cm^{-1} also occurs within the range possible for ν_4 of BF_4^-; however, it is not assigned to BF_4^-. This is based on band intensity comparison of spectra, containing varying amounts of other BF_4^- salts in addition to $ClF_2^+BF_4^-$. It is not possible to eliminate a possible contribution of ν_2 of ClF_2^+ to the band at 519 cm^{-1} (the splitting of ν_2 of ClF_2^+ into two bands will be discussed later).

The remaining bands observed in the spectra of both $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$ complexes should be due to ClF_2^+. A symmetric triatomic ion of the type XY_2^+, such as ClF_2^+, could be either linear or bent. Linear XY_2^+ has symmetry $D_{\infty h}$. The three normal modes of vibration are classified as $\Sigma_g^+ + \pi_u + \Sigma_u^+$. Since linear XY_2^+ has a symmetry center, it follows the rule of mutual exclusion. Therefore, π_u and Σ_u^+ will be only infrared active and Σ_g^+ only Raman active. Bent XY_2^+ has symmetry C_{2v}. The three normal modes of vibration are classified as $2\,A_1 + B_1$. All three modes will be infrared and Raman active.

Since, in the case of ClF_2^+, two Raman- and three infrared-active vibrations are observed, and the rule of mutual exclusion is not followed, the possibility of symmetry $D_{\infty h}$ is eliminated. The observation of only two Raman lines for ClF_2^+ instead of three (required for bent XY_2^+) can be explained by the small frequency difference between the antisymmetric and symmetric stretching vibration, as indicated by the infrared spectra. Since the intensity of the antisymmetric stretching mode should be rather low in the Raman spectrum, this line might be masked by the very strong symmetric vibration, observed at 811 cm^{-1}. In addition, the slit width of the Raman spectrophotometer had to be increased to obtain the proper intensity for the spectrum of the solid, thus resulting in loss of resolution. The latter may also account for the fact that only one Raman line was observed at 544 cm^{-1} whereas a doublet was observed in the infrared spectrum of $ClF_2^+AsF_6^-$ at 558 and 520 cm^{-1}. These two bands are the only ones which have counterparts in the infrared spectrum of $ClF_2^+BF_4^-$. Therefore, they are

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assigned to the deformation mode of ClF_2^+ (the splitting into two bands will be discussed later). Thus, we can account for the correct number (three) of fundamental vibrations for ClF_2^+, active in both the infrared and the Raman spectrum with good agreement of the frequencies as expected for symmetry C_{2v}. Consequently, these results leave no doubt that the ClF_2^+ cation is bent.

There are four very weak bands in the infrared spectrum of $ClF_2^+AsF_6^-$ yet unassigned. They are all of too low intensity and occur at too high frequencies for fundamental vibrations. Whereas the two doublets at 1624, 1610 cm^{-1} and 1312, 1297 cm^{-1} can be assigned to the combination vibrations, $\nu_1 + \nu_3$, of ClF_2^+, and $\nu_2 + \nu_4$, of AsF_6^-, respectively, it is not clear if the two very weak bands at 1130 and 976 cm^{-1} are due to $ClF_2^+AsF_6^-$ or are caused by trace impurities.

Three bands in the infrared spectrum of $ClF_2^+BF_4^-$ are yet unassigned, two weak doublets at 1610, 1575 cm^{-1} and 1289, 1305 cm^{-1}, and a band of medium intensity at 766 cm^{-1}. The doublet at 1610, 1575 cm^{-1} can be assigned to the combination, $\nu_1 + \nu_3$, of ClF_2^+ in analogy to the 1624, 1610 cm^{-1} doublet in ClF_2^+-AsF_6^-. The other two bands are due to BF_4^- (compare with the spectrum of $K^+BF_4^-$).[21-23] The doublet at 1289, 1305 cm^{-1} is considered the combination band, $\nu_1 + \nu_4$, while the band at 766 cm^{-1} is assigned to the symmetric stretching vibration, ν_1, of BF_4^-. This mode should be inactive in the infrared spectrum according to the selection rules for T_d symmetry. However, in the crystalline state two effects may cause deviations from ideal conditions: (i) The site symmetry of a group within a crystal may be lower than the symmetry of the group itself. Thus, either activation of normally inactive vibrations (in either the infrared or the Raman spectrum) can result or degenerate vibrations can split into their nondegenerate components owing to the variation of the selection rules. (ii) If there is more than one group of a certain species within the unit cell of a crystal, a splitting of bands may occur because of in-phase and out-of-phase motions of these groups. Both effects are observed in the infrared spectrum of $K^+BF_4^-$[21-23] and should also occur in the case of $ClF_2^+BF_4^-$. This deviation from the ideal spectrum of the undisturbed ions should be even greater for $ClF_2^+BF_4^-$ than for $K^+BF_4^-$ owing to the lower symmetry of ClF_2^+ compared with that of spherical K^+. This explains the higher intensity of ν_1 of BF_4^- in the spectrum of $ClF_2^+BF_4^-$ compared with the weak band observed in the spectrum of $K^+BF_4^-$.

Similar conditions apply to $ClF_2^+AsF_6^-$. It is known from X-ray studies that the AsF_6^- octahedron is distorted in $K^+AsF_6^-$.[24,25] In addition, ν_2 (E_g) of AsF_6^- is also observed in the infrared spectra of $AsCl_4^+AsF_6^-$[19] and of $NF_4^+AsF_6^-$,[20] contrary to the selection rules. Further evidence for the selection rules not being strictly applicable in $ClF_2^+AsF_6^-$ is the occurrence of two shoulders for the infrared-active ν_4 band of AsF_6^-. This indicates an annulment of the degeneracy of ν_3 (F_{1u}). The shoulder on the low-frequency side of this band may also be interpreted as coinciding with ν_1 (A_{1g}) in the Raman spectrum. The splitting of the deformation mode of ClF_2^+, ν_2, in the infrared spectrum of $ClF_2^+AsF_6^-$ (and perhaps also in that of $ClF_2^+BF_4^-$ if the band at 519 cm^{-1} contains some contribution from ν_2 of ClF_2^+) may be interpreted as a coupling effect of more than one ClF_2^+ group within the unit cell of the crystal.

The possibility of interpreting the vibrational spectra in terms of asymmetric bent ClF_2^+ should be discussed briefly, since this type of cation, having C_s symmetry, would also exhibit three fundamental vibrations, active in both the infrared and Raman spectrum. The ClF_2^+ cation is formed from ClF_3 by the abstraction of F^-. Since ClF_3 exhibits two types of Cl–F bonds,[26] one shorter and two longer ones, it could be assumed that the weaker bond breaks first resulting in asymmetric bent ClF_2^+ provided no electronic relaxation occurs. However, the following arguments render this structure most unlikely: (i) The force constants of the two different types of Cl–F bonds in ClF_3 differ considerably (3.99 and 2.85 mdynes/A).[27] If no electronic relaxation occurs, ν_1 and ν_3 of resulting asymmetric ClF_2^+ should exhibit a large frequency difference. The closeness of the observed frequencies, 818 and 810 cm^{-1} for ν_3 and ν_1, respectively, disagrees with this model. The possibility of assigning the bands at about 810 and 540 cm^{-1} to ν_3 and ν_1, respectively, and of explaining the splitting of the 810-cm^{-1} band by Fermi resonance between $2\nu_2$ and ν_3, should result in a frequency of about 405 cm^{-1} for ν_2. However, no evidence can be found, in either the Raman spectrum of ClF_2^+-AsF_6^- or the infrared spectrum of $ClF_2^+BF_4^-$, for the existence of such a band in this frequency range. (ii) The known symmetric structure of ICl_2^+[28] suggests a similar configuration for ClF_2^+ owing to their isoelectronicity. (iii) The observation of a combination band at about 1610 cm^{-1} in the infrared spectra of both $ClF_2^+AsF_6^-$ and $ClF_2^+BF_4^-$, corresponding to $\nu_1 + \nu_3$ of ClF_2^+, suggests a value of about 800 cm^{-1} for ν_1. (iv) The infrared spectrum of $ClF_2^+AsF_6^-$, recorded at room temperature, corresponds to the low-temperature spectra. It seems unlikely that the activation energy for an electronic relaxation would be so high that this relaxation would occur only at temperatures higher than 25°. Based on these arguments as well as bond theory considerations, the asymmetric bent model can be ruled out.

The strong influence of crystal field effects might apply as well to the ClF_2^+ cation as it does to the anions. In this case the selection rules might not strictly apply to ClF_2^+ and thus the number of infrared and Raman bands and their coinciding would not be a strong argument in favor of the bent C_{2v} model. However, even

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(25) J. A. Ibers, *ibid.*, **9**, 967 (1956).
(26) R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, **27**, 981 (1957); D. F. Smith, *ibid.*, **21**, 609 (1953).
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(28) C. G. Vonk and E. H. Wiebenga, *Acta Cryst.*, **12**, 859 (1959).

under these conditions, the following argument strongly supports the proposed bent structure. If the central X atom in linear XY_2 is not much heavier than the Y atoms, the symmetric and antisymmetric stretching vibrations have very different frequencies owing to the strong coupling between the two oscillators in a linear combination. For example, the frequency difference found for the stretching vibrations of linear ClF_2^- [9] is 160 cm^{-1}. On the other hand, if the two oscillators form an angle of 90° and the coupling of the symmetric stretching vibration with the deformation mode of the same species is neglected, ideally, both stretching vibrations should have identical frequencies. For example, SCl_2, having a Cl–S–Cl angle of about 100°, shows a stretching vibration frequency difference of 21 cm^{-1}.[29] Since the stretching vibrations in ClF_2^+ show only a frequency difference of about 8 cm^{-1}, the F–Cl–F angle should not be much larger than 90° and a linear structure can definitely be ruled out. The bent structure of ClF_2^+ is further supported by the results obtained from the force constant calculations.

Two possible models for the bent structure of ClF_2^+ are: (i) A hybridization model, assuming sp^3 hybridization of the orbitals of the chlorine atom resulting in a tetrahedral arrangement (a slight decrease of the F–Cl–F bond angle from 109° 27′ can be expected, since the repulsion of one fluorine atom by the two free electron pairs should be stronger than that exerted by the other fluorine atom), and (ii) a model, involving only localized p orbitals of the chlorine atom resulting in two covalent p–σ bonds. The expected F–Cl–F bond angle of 90° could be slightly increased by mutual repulsion of the two fluorine atoms. An increase of the F–Cl–F bond angle can also be expected, if the Cl–F bonds have partial double-bond character. In the case of ClF,[30] for example, an increase in the bond strength over the calculated single-bond value has been proposed. Since the valence force constant of ClF_2^+ (4.77 ± 0.07 mdynes/A) is even somewhat higher than that of ClF (4.364 mdynes/A),[31] partial double-bond character is also possible for ClF_2^+. The upper limit for this type of angle widening may be derived from the known SO_2 bond angle (120°). Therefore, the force constants of ClF_2^+ were calculated for an F–Cl–F bond angle varying from 90 to 120°, thus covering the range considered theoretically possible. The value obtained for a linear structure (180°) is also given for comparison. Table II shows the strong influence of the F–Cl–F bond angle on the coupling constant, f_{rr}, between the two Cl–F bonds. In contrast, the valence force constant increases only slightly, and the coupling and deformation constants, $f_{r\alpha}$ and f_α, respectively, decrease only slightly with an increase of the bond angle. Normally, the value of the coupling force constant, f_{rr}, does not exceed about 15% of the valence force constant. For linear ClF_2^+, however, f_{rr} would be 34% of f_r (for linear ClF_2^-, for example, f_{rr} is only 7% of f_r).[9] There are some special cases, in which such large coupling constants have been observed;[32] however, they should be accompanied by a simultaneous decrease of the valence force constant by about 50% when compared with the covalent single-bond values. Therefore, this explanation is not applicable to ClF_2^+, because of its large valence force constant, comparable to that of ClF.[31] On this basis we can also rule out the linear model, involving only one delocalized p orbital of the chlorine atom, for the formation of a three-center–four-electron (3c–4e) semiionic p–σ bond.[33–35] This is in good agreement with theoretical considerations, energetically favoring models i and ii over the semiionic 3c–4e bond model in the case of ClF_2^+ since its chlorine atom has only eight valence electrons. Therefore, model i or ii does not require any unshared electron pair to occupy either a d orbital or a hybridized orbital with a relatively high d contribution. In all other known chlorine–fluorine-containing compounds, with the exception of ClF, the central chlorine atom has more than eight valence electrons, and, consequently, the semiionic 3c–4e bond model becomes energetically more favorable for binding an even number of fluorine atoms.

For a F–Cl–F bond angle of 120° in ClF_2^+, f_{rr} amounts to 14% of f_r, just within the above-mentioned limit. For angles smaller than 96°, f_{rr} becomes negative. Although small negative values of f_{rr} are rather unusual, they cannot be entirely ruled out. Thus, it cannot be decided on the basis of the force constant calculation whether the hybridization or the localized covalent p–σ bond model is correct. However, model ii is considered somewhat more likely by comparison with isoelectronic ICl_2^+.[28] The ICl_2^+ cation has a bond angle of 92.5° in $ICl_2^+SbCl_6^-$.

Since the valence force constant, f_r, of ClF_2^+ shows only a slight dependence on the variation of the bond angle, a value of 4.77 ± 0.07 mdynes/A seems to be reliable. This value is somewhat higher than that of ClF.[31] This may be explained by the difference in number of free electron pairs on the chlorine atoms.[30] If this effect is taken into consideration for evaluating the single-bond values,[30,36] the calculated bond orders, N, are identical for ClF and ClF_2^+ (1.50 and 1.51, respectively). Since the bonding in ClF can be explained by a simple p–σ bond model[37] and the bond orders in ClF and ClF_2^+ are very similar, the localized p–σ bond model from this point of view also seems to be more likely than the hybridization model. Although the obtained N values are certainly too high, some contribution from double-bond structures cannot be ruled out for ClF_2^+ and ClF.[30] The formation of these partial double bonds is possible since the chlorine

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atom has unoccupied d orbitals. The polarity of the ClF bond due to the electronegativity difference between the chlorine and fluorine atom may be compensated to some extent by the formation of partial double bonds. The bond order calculations also show that the bond order of ClF_2^- (0.92) is considerably lower than that of ClF and ClF_2^+ and is best explained by the semiionic 3c–4e bond model. This is in good agreement with theoretical expectation,[32,33] predicting for localized covalent bonds a bond order of about 1, and for 3c–4e bonds bond orders of about 50% of the single-bond value. If it is realized that the N values calculated for ClF, ClF_2^+, and ClF_2^- are all somewhat too high, the force constants seem to be a useful method for distinguishing between these two different types of bonding. A positive or negative charge on the central chlorine atom will obviously also have some influence on the type of bonding. Whereas a negative charge will favor the contribution of ionic structures to the bond energy and thus the formation of semiionic bonds, a positive charge will increase the electronegativity of the central chlorine atom and increase the covalent contribution.

Acknowledgment.—We thank Drs. A. E. Pavlath and J. P. Guertin for their helpful support and Dr. A. C. Jones of Shell Development, Emeryville, Calif., for the use of the Raman spectrophotometer.

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Photoinduced Reactions in Solid Carbon Suboxide

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Received August 10, 1966

The infrared spectrum of the photolysis products of C_3O_2 in a solid film at ~100°K has been analyzed for clues to the mechanism of photopolymerization of C_3O_2 This spectrum consists of several sharp bands with the most characteristic features centered at 2060, 1822, 1716, and 1697 cm^{-1}. The richness of the spectrum combined with the insensitivity of band positions or relative intensities to either extent of photolysis or the wavelength of photolytic radiation hints at a single reaction path initiated by cleavage of C_3O_2 and culminating in a tricyclic ring compound $C_{13}O_8$. Upon warming, the $C_{13}O_8$ molecules then act as nucleation sites for polymerization.

Introduction

The photoinduced gas-phase reaction of C_3O_2 with ethylene has been interpreted by Bayes[1] as resulting from cleavage of C_3O_2 to give the carbene, C_2O, which subsequently attacks the ethylene double bond. The resultant ring compound then rearranges to give the observed reaction products. The attractiveness of this mechanism has further increased since Jacox, *et al.*,[2] detected C_2O in the photolysis products of C_3O_2 trapped in an inert gas matrix at liquid helium temperatures. The latter study also indicated that C_2O is mobile in such matrices at temperatures greater than ~20°K.

One might thus expect that photolysis of a pure thin film of C_3O_2 at 100°K would yield mobile C_2O species, which, by analogy with Bayes' proposal, would attack neighboring C_3O_2 molecules to give the three-membered ring compound C_5O_3. In a very recent paper Smith, *et al.*,[3] suggest C_5O_3 as an intermediate in the gas-phase photopolymerization of C_3O_2 but the species has not been detected. We report here the results of spectral studies of the products of photolysis of thin films of pure C_3O_2 at ~100°K.

Experimental Section

C_3O_2 was prepared by allowing P_2O_5 and malonic acid to react at 140°. The product mixture was distilled through an Ascarite column and purified by several single-state vacuum distillations until no impurity bands were detectable in the infrared spectrum of a thick solid film. Initially we planned to conduct the photolysis with the C_3O_2 molecules isolated in a CO_2 matrix at 100°K using various CO_2:C_3O_2 ratios to sort out the reaction steps which occur. However, consistent with the observation of Moll and Thompson at 4.2°K,[4] no detectable reaction could be induced while using a medium-pressure mercury lamp as a source of photolytic radiation as long as the ratio was 5 or greater. Therefore, our attention was directed primarily to pure thin films of C_3O_2.

The pure C_3O_2 was thus slowly deposited on a cold (100°K) sodium chloride window suspended in a standard low-temperature infrared cell. Deposition rates were controlled by throttling through a needle valve such that deposition times varied from a few minutes to 1 hr, depending upon the film thickness desired. After an infrared scan of the pure thin film, photolysis was initiated using a medium-pressure mercury lamp mounted flush against one portal of the low-temperature cell. In several instances the lamp output was filtered using solution filters. A given deposit was alternately photolyzed and scanned with succeeding photolysis periods of increasing length. Thus monitoring of samples photolyzed for periods ranging from 0.5 to 27 hr was possible. In a few instances the effect of warming the photolyzed C_3O_2 was followed spectroscopically. All infrared spectra were recorded on a Beckman IR-7 spectrometer.

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